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Derivation of Atomic Co-ordinates in Helical Structures

A Single-Crystal Adaptor for the Norelco High-Angle Diffractometer

Technical Reports 71 and 72
Laboratory for Insulation Research
Massachusetts Institute of Technology

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Technical Report 71

Derivation of Atomic Co-ordinates in Helical Structures

by

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DERIVATION OF ATOMIC CO-ORDINATES IN HELICAL STRUCTURES

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Abstract: A general method is developed for obtaining the co-ordinates of atoms in helical structures. The helix is treated as the repetition of a structural unit by an n -fold screw axis, where n is continuously variable instead of being restricted to integral values. Expressions for evaluating the co-ordinates in terms of an orthogonal axial system are derived, and graphs which facilitate the use of these expressions are given.

All crystal structures belonging to space groups which contain screw axes can be formally considered as helical structures. In the case of n -fold screw axes where n is an integer with values 2, 3, 4 or 6, the co-ordinates of the atoms which are repeated by the screw can be obtained quite simply in terms of the co-ordinates of general and special positions for the appropriate space group. These co-ordinates are listed in Vol. I of the International Tables for X-Ray Crystallography (1952).

In more complex structures such as proteins, however, in which it is possible that there may be helices approximating the repetition of structural units by n -fold screw axes where n is nonintegral, the co-ordinates of atoms in successive units cannot be readily listed, since n is continuously variable. The co-ordinates are needed, however, for calculations of bond lengths and bond angles, and, since they vary smoothly with changes in n , graphs can be drawn

which greatly reduce the amount of work involved in obtaining the co-ordinates for a given structural unit repeated by an n -fold screw axis for a particular choice of n .

The need for a systematic derivation of this type was recognised by Dr. Barbara W. Low of Harvard Medical School, in the course of her work on proteins, and the specific form in which the derivation is given below was developed to analyse polypeptide chain helices.¹⁾ This concept can be adapted easily to deal with structures containing infinite chains, such as Te and Se, or with the small deviations from true screw symmetry involved in spiral distortion in crystals which contain screw axes, such as quartz. The mathematical derivation of it is therefore given below.

Consider first the structural unit which is to be repeated by the screw axis (in this case the residue $\cdot C_1 \cdot C_1' O_1 \cdot N_1 H_1 \cdot C_2 \cdot$, which is shown inscribed in a circle of diameter $C_1 C_2$ in Fig. 1). The residue is assumed to be planar, and its plane is always taken to be parallel to the helical axis. Relaxation of this condition may be introduced later on in the calculation.

If one end, C_1 , is kept fixed, the residue may be tilted either up or down. If P is the pitch of the final coil, i.e., the vertical translation per complete turn, and n is the number of residues per complete turn, then, in a given helix, this vertical translation per residue is P/n . If the residue is tilted upwards so that $C_1 C_2^*$ (solid line) is its horizontal projection (normal to the helical axis), then the CO and NH groups are almost vertical and parallel to the helical axis. A value of $P/n = 1.4 \text{ \AA}$ was used to construct Fig. 1.

When the residue is tilted downwards, so that $C_1 C_2^*$ (broken line) is horizontal, then the CO and NH groups are both sharply inclined to the helical axis,

1) B. W. Low and H. J. Grenville-Wells, "Generalized Mathematical Relationships for Polypeptide Chain Helices. The co-ordinates of the π helix," Proc. Nat. Acad. Sci. Wash., 1953, in press.

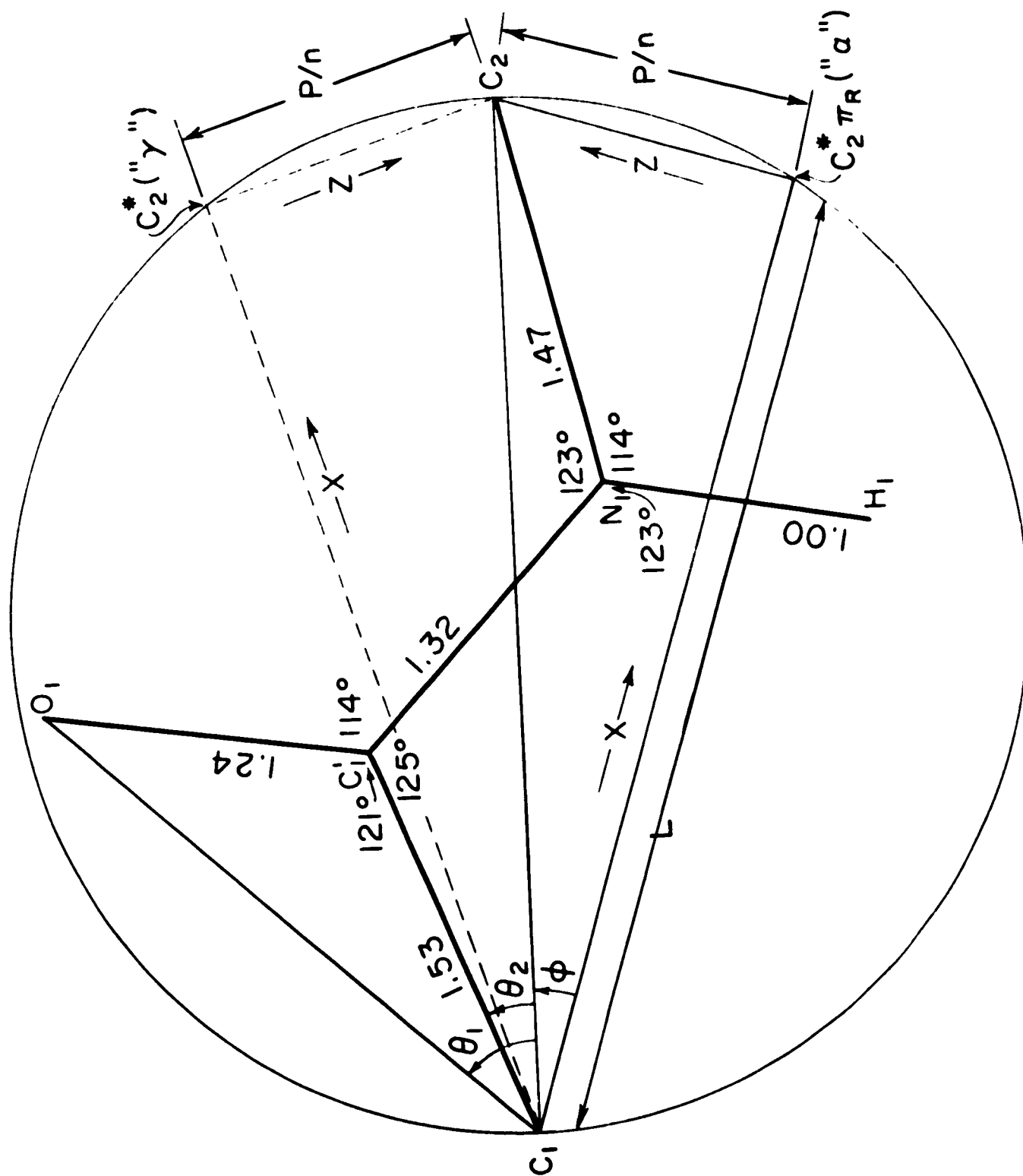


Fig. 1. Fundamental unit to be repeated by the screw axis.

whereas C_1C_1' and N_1C_2 are nearly parallel to $C_1C_2^*$.

It should be noted that these two directions of tilt define two different helices, which nevertheless have the same value of P/n . Systematic variation of P/n will therefore result in two distinct series of helices, which cannot be transformed into one another by winding more tightly or more loosely.

This will always be true unless the line C_1C_2 is a mirror line in the structural unit, in which case the upward and downward tilts associated with a particular value of P/n produce the enantiomorphous pair of helices corresponding to a left-handed and right-handed screw. This is not the case for the residues of polypeptide chains, so that two series, which we have called the "α" and "γ" series because they contain Pauling's "α" and "γ" helices,²⁾ respectively, must be considered.

Atomic co-ordinates for all atoms in the helix are derived in two stages: (1) the co-ordinates of atoms in the basic structural unit are obtained with the fixed end of the unit taken as origin (C_1 in Fig. 1); (2) the co-ordinates of atoms in successive units are obtained by the operation of the n -fold screw on these "basic" co-ordinates.

First stage. If the basic unit is placed in the plane $y = 0$, only the x and z co-ordinates remain to be determined. (If a nonplanar unit is to be considered, this would no longer be true.)

It can be seen in Fig. 1 that for a given structural unit, the angles $\theta_1, \theta_2, \dots$ and the distances of the atoms from the origin C_1 , i.e., C_1C_1', C_1O_1, \dots are fixed; and when a ratio P/n has been decided upon, the pair of positions C_2^* , which must lie on the circle C_1C_2 , are also fixed, together with the directions of the x and z axes and the angle of tilt $\phi = P/(nL)$. Hence the co-ordinates will be given by expressions of the form

2) L. Pauling, R. B. Corey and H. R. Branson, Proc. Nat. Acad. Sci. Wash. 37, 205 (1951).

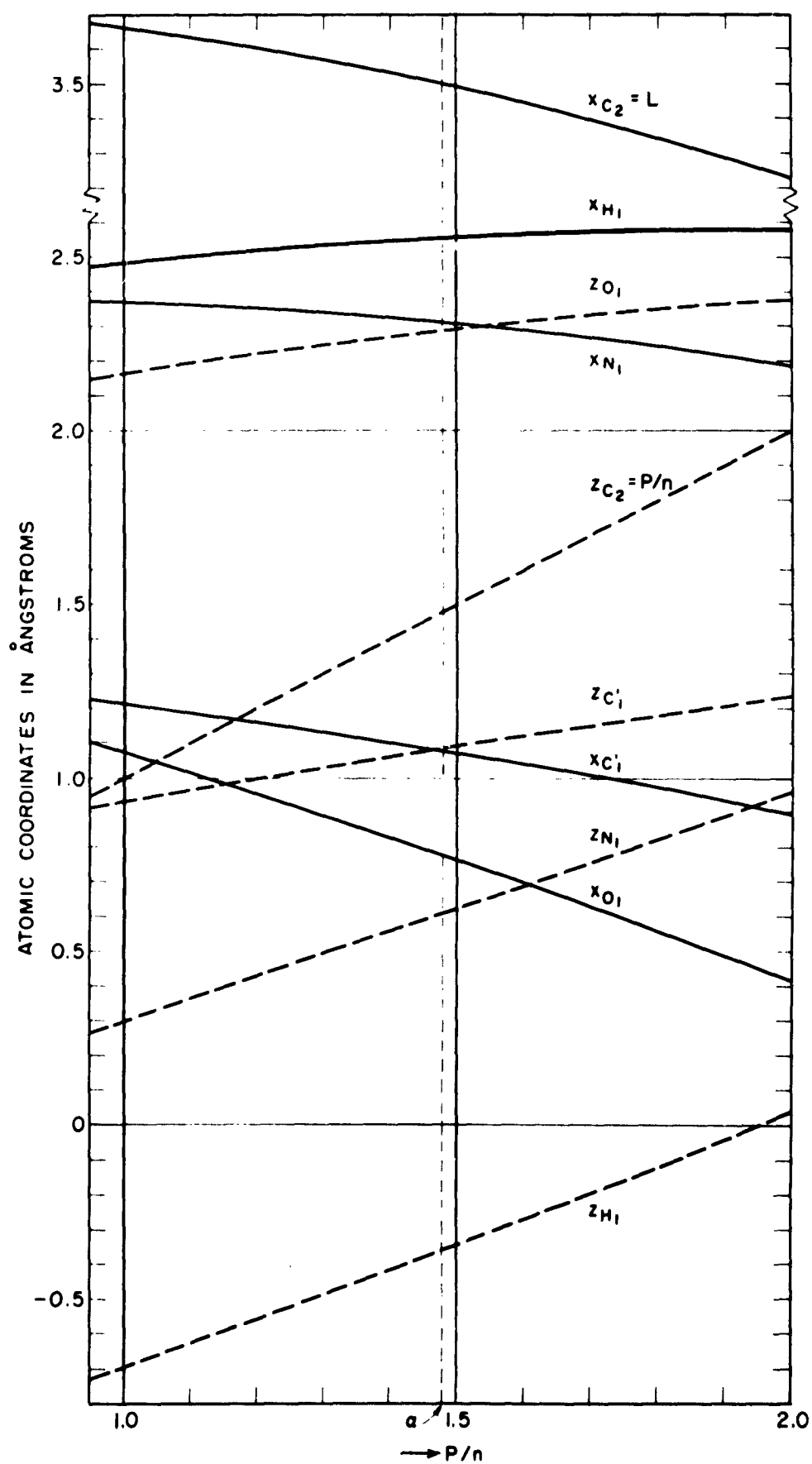


Fig. 2. Graph showing atomic co-ordinates in the fundamental unit as functions of P/n .

$$\begin{aligned}
 x_{C_1} &= 0 & z_{C_1} &= 0 \\
 x_{O_1} &= C_1 O_1 \cos (\phi + \theta_1) & z_{O_1} &= C_1 O_1 \sin (\phi + \theta_1) \\
 x_{C'_1} &= C_1 C'_1 \cos (\phi + \theta_2) & z_{C'_1} &= C_1 C'_1 \sin (\phi + \theta_2) \\
 x_{C_2} &= C_1 C_2 \cos \phi = L & z_{C_2} &= C_1 C_2 \sin \phi = P/n \\
 &= \text{projected length of unit}
 \end{aligned}$$

for the series of helices with an upward tilt, while in the other series the signs of the angles $\theta_1, \theta_2 \dots$ will be reversed.

All these co-ordinates will be smooth functions of ϕ , and hence of P/n , and may therefore be plotted against P/n for the range of values to be considered, as has been done in Fig. 2. Values of the co-ordinates for the ratio $P/n = 1.48$ lie on the dotted line a .

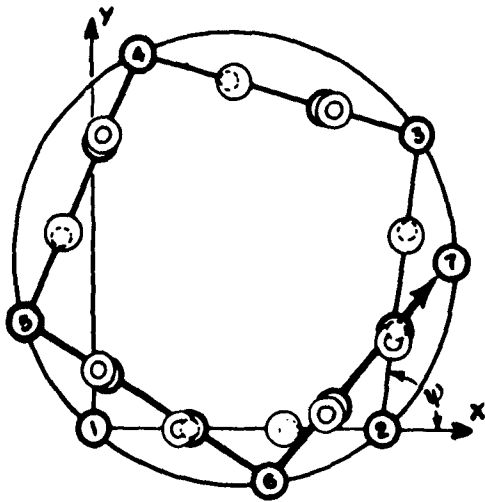


Fig. 3. Helix projected on a plane perpendicular to the helical axis.

Second stage. Figure 3 shows the helix projected on a plane perpendicular to the helical axis. The vertical plane containing each structural unit becomes a line of length L , and the angle between two such lines is the helical angle $\psi = 360/n$, and is independent of the pitch P . Since these lines are equidistant from the helical axes, their ends $C_1, C_2, C_3 \dots$ lie on the circumference of a circle of radius

$$R = \frac{1}{2} L \operatorname{cosec} \psi/2. \quad (1)$$

The co-ordinates of the origin of the r th unit are thus

$$x_{C_r} = L [0 + 1 + \cos \psi + \cos 2\psi + \dots + \cos (r-2)\psi] \quad (2a)$$

$$y_{C_r} = L [0 + 0 + \sin \psi + \sin 2\psi + \dots + \sin (r-2)\psi] \quad (2b)$$

$$z_{C_r} = (r-1) P/n.$$

The co-ordinates of the point p_r in the r th unit are given by

$$x_{p_r} = x_{C_r} + x_{p_1} \cos (r - 1) \psi \quad (3a)$$

$$y_{p_r} = y_{C_r} + x_{p_1} \sin (r - 1) \psi \quad (3b)$$

$$z_{p_r} = (r - 1) P/n + z_{p_1} \dots \quad (3c)$$

Equations (2a) and (2b) can be rewritten in the form

$$x_{C_r} = L u_r \dots \quad (4a)$$

$$y_{C_r} = L v_r \dots \quad (4b)$$

where u_r and v_r are the unitary co-ordinates of the origins of successive units, i.e.,

$$u_r = [1 + \cos \psi + \cos 2\psi + \dots + \cos (r - 2) \psi] \quad (5a)$$

$$v_r = [\sin \psi + \sin 2\psi + \dots + \sin (r - 2) \psi] \quad (5b)$$

These functions are shown in Fig. 4 for $r = 2, 3, 4, 5, 6$ over the range $n = 3.0$ to 5.5.

Equations (3a) and (3b) may be rewritten

$$x_{p_r} = L u_r + A_r x_{p_1} \dots \quad (6a)$$

$$y_{p_r} = L v_r + B_r x_{p_1} \dots \quad (6b)$$

where $A_r = \cos (r - 1) \psi$ and $B_r = \sin (r - 1) \psi$. Values of A_r and B_r for $r = 2$ to 6 are shown in Fig. 5 for the range $n = 3.0$ to 5.5.

Hence, to determine atomic co-ordinates in the r th unit in a helix of pitch P with an n -fold screw: (a) the co-ordinates x_{p_1} and z_{p_1} in the basic unit and the value of L for the requisite value of P/n are obtained from Fig. 2; (b) the values of u_r and v_r obtained from Fig. 4 for the chosen value of n and multiplied by L ; (c) the values of A_r and B_r are obtained from Fig. 5 for the chosen value of n and multiplied by the value of x_{p_1} ; (d) the co-ordinates are written down from Eqs. (6a), (6b) and (3c).

Since the co-ordinates have been obtained in an orthogonal system, bond lengths and bond angles can be determined from the usual expressions, so that

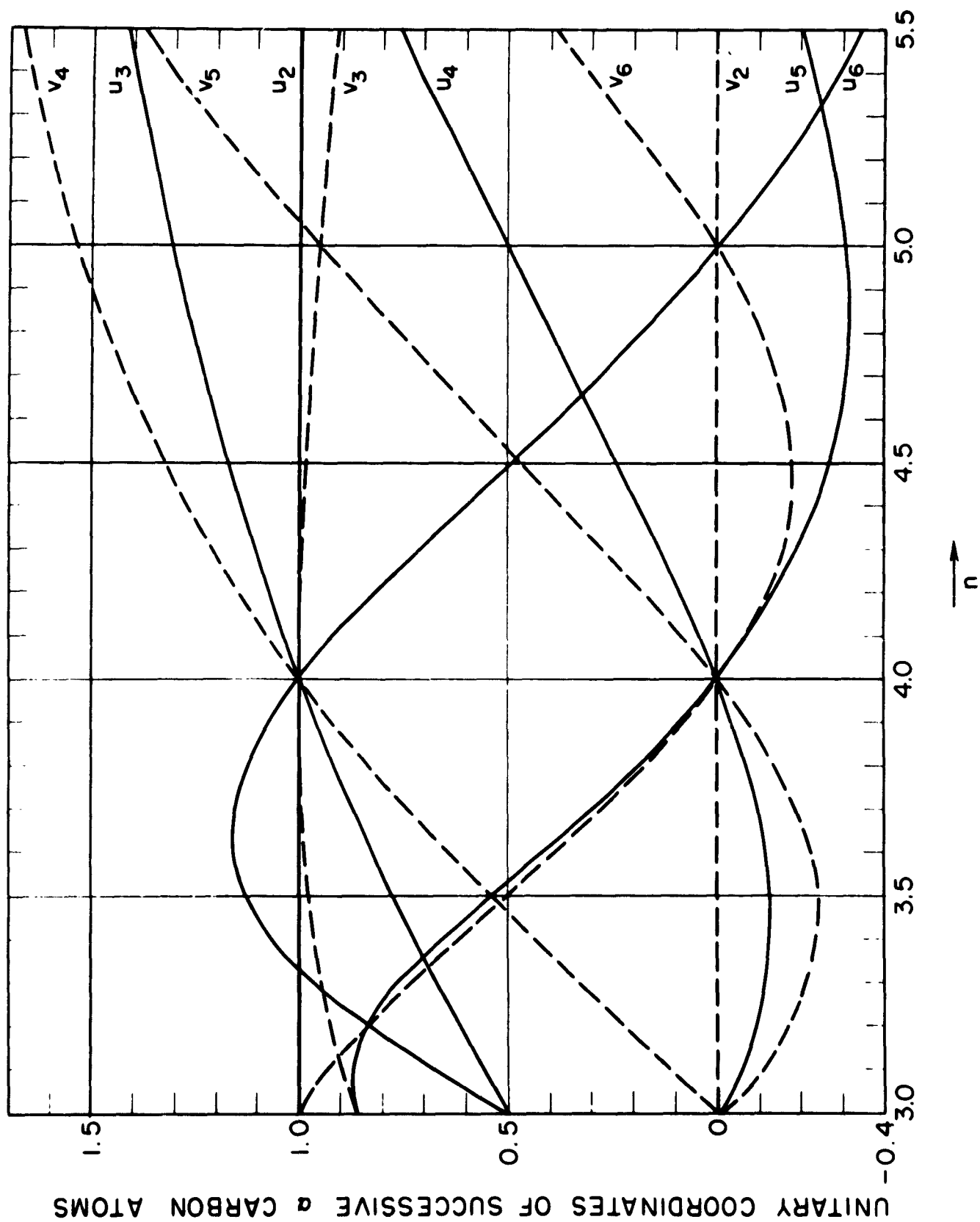


Fig. 4. Unitary co-ordinates of origins of successive structural units as functions of n .

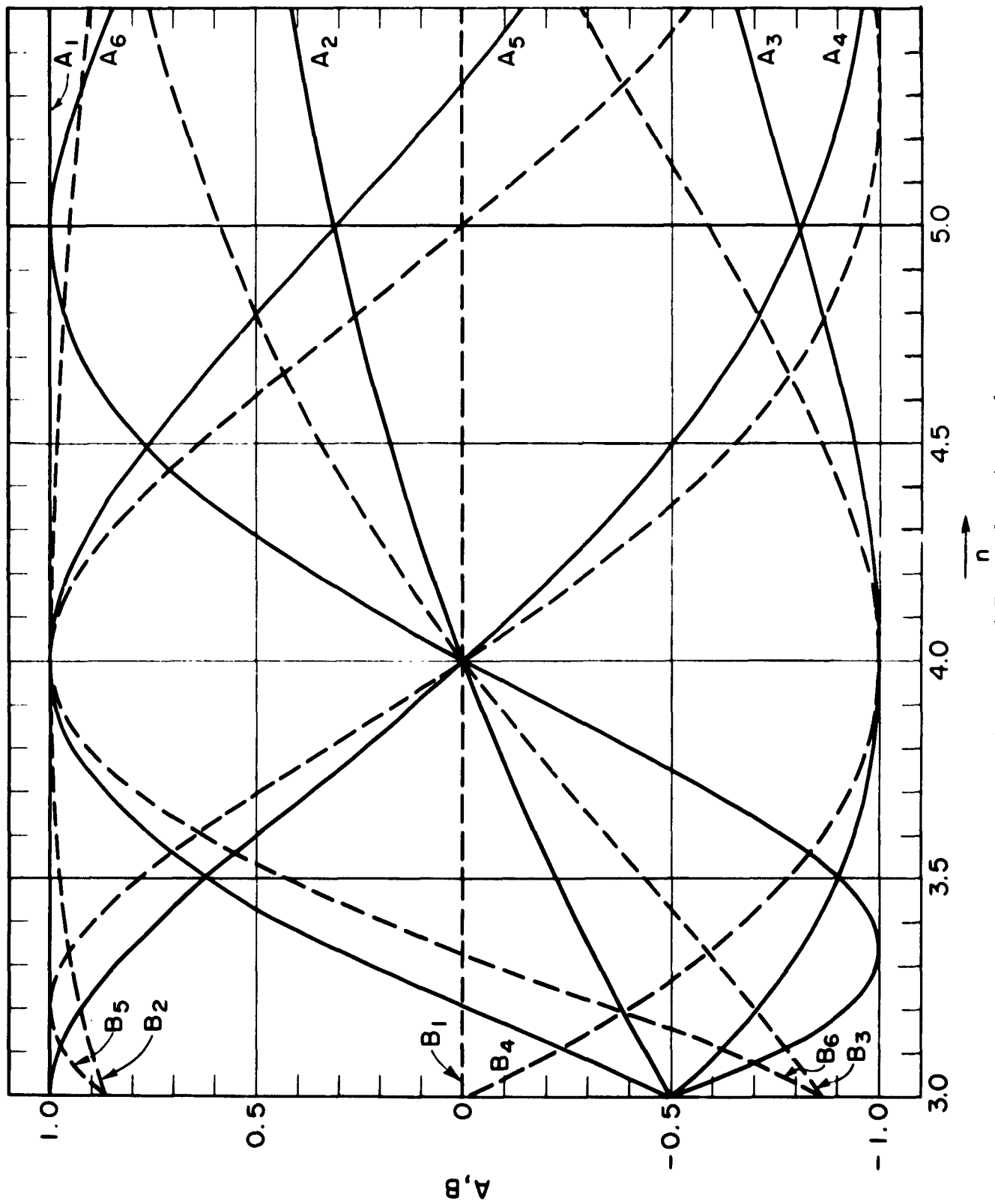


Fig. 5. A_r and B_r as functions of n .

the distance $D_{1,2}$ between two atoms at $(x_1 y_1 z_1)$ and $(x_2 y_2 z_2)$ is given by

$$D_{1,2}^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2,$$

and the angle δ subtended at $(x_2 y_2 z_2)$ by the atoms at $(x_1 y_1 z_1)$ and $(x_3 y_3 z_3)$ is given by

$$\cos \delta = \frac{(x_3 - x_2)(x_2 - x_1) + (y_3 - y_2)(y_2 - y_1) + (z_3 - z_2)(z_2 - z_1)}{D_{3,2} \cdot D_{2,1}}.$$

These expressions can be rewritten in various ways in terms of the values of x, y and z given by Eqs. (6a), (6b) and (3c) as a specific problem may require.

For some purposes, such as the calculation of the radial distribution function, it may be preferable to express the atomic positions in terms of cylindrical co-ordinates, with the origin of the co-ordinate system taken on the helical axis.

As can be seen in Fig. 3, all the atoms of a particular type lie on a circle

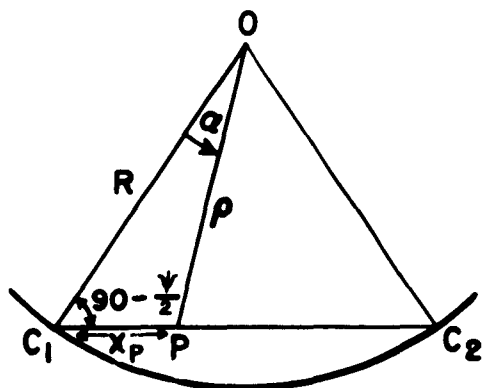


Fig. 6. Nomenclature for polar co-ordinates.

of a particular radius, and it can be seen from Fig. 6 that this radius ρ is given by

$$\begin{aligned} \rho_p^2 &= R^2 + x_p^2 - 2Rx_p \cos(90 - \psi/2) \\ &= R^2 + x_p^2 - 2Rx_p \sin(\psi/2). \end{aligned}$$

$$\text{But } R = \frac{1}{2} L \operatorname{cosec}(\psi/2),$$

$$\therefore \rho_p^2 = \frac{L^2}{4 \sin^2(\psi/2)} + x_p^2 - Lx_p.$$

And if OC is taken as the line $a = 0$, then

$$a_p = \sin^{-1} \left[\frac{(x_p \cos(\psi/2))}{\rho_p} \right].$$

The foregoing section gives analytical

expressions for the co-ordinates of the atoms in the helix. It can be seen in Fig. 7, however, that if, in addition to the circle of diameter $C_1 C_2$ drawn in Fig. 1, circles having diameters $C_1 O_1$, $C_1 C'_1$, $C_1 N_1$ and $C_1 H_1$ are also drawn, any choice of P/n , which fixes the points $C_2^*(a)$ and $C_2^*(y)$ results in a line $C_1 C_2^*$ which cuts the extra circles at the points O_1^* , C'_1^* , etc.

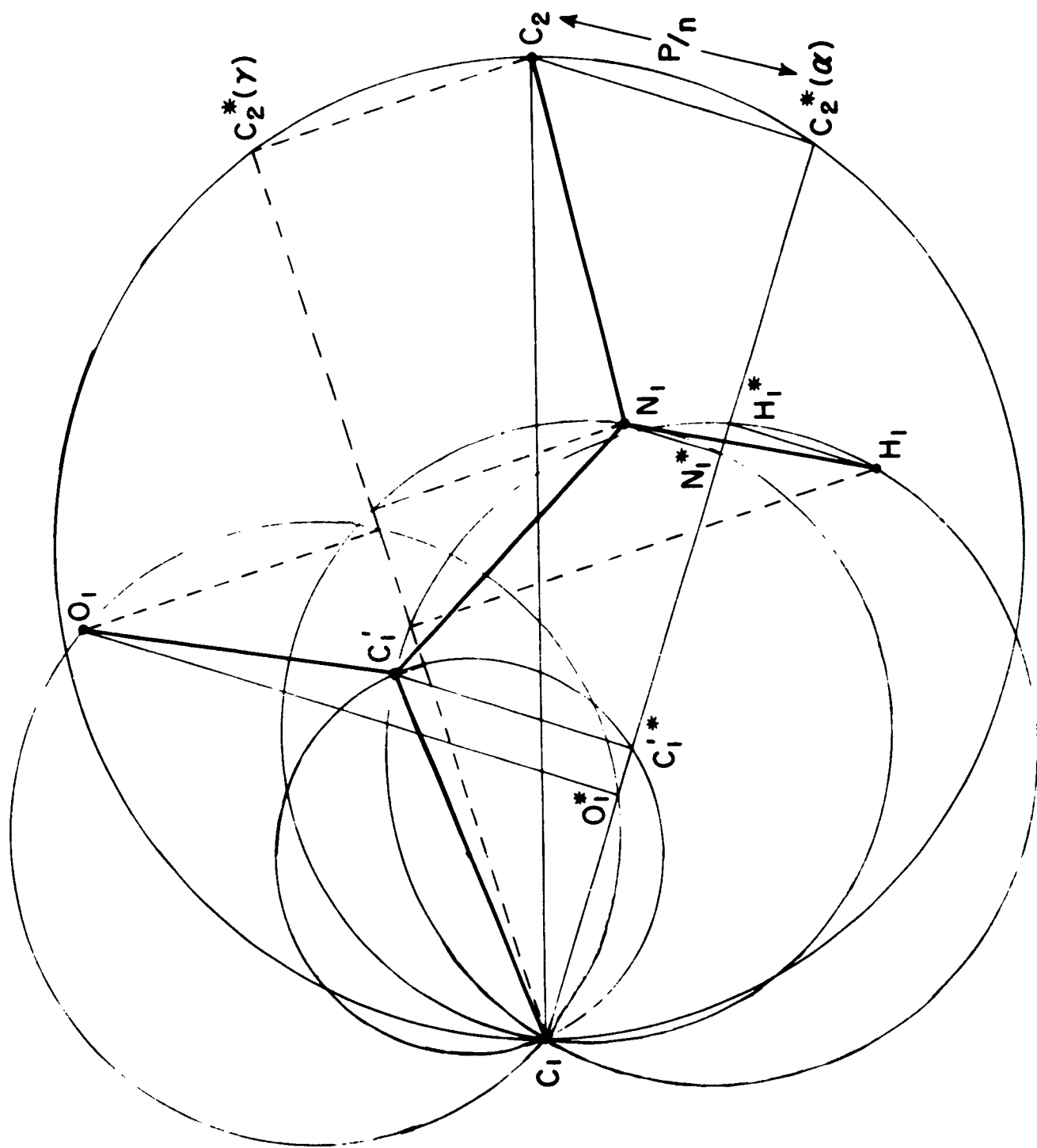


Fig. 7. Graphical derivation of atomic co-ordinates in the fundamental unit.

Hence the lengths $C_1O_1^*$, $C_1H_1^*$ etc., are the x co-ordinates, and $O_1O_1^*$, $H_1H_1^*$, etc., are the z co-ordinates in the basic unit. Co-ordinates of atoms in successive units can be obtained either by utilizing Figs. 4 and 5, or graphically by constructing the projection of the helix, and reading the co-ordinates directly by superposing the tracing on a sheet of graph paper.

However, since the construction of such a helix involves the repetition several times of selected constants, such as the helical angle, it is particularly liable to cumulative errors; hence, while a graphical construction is valuable as an aid to visualizing the general feasibility of a postulated helix, it does not seem suitable for obtaining accurate values of the co-ordinates.